The stripe phase of the β-INC-α transformation of quartz under a uniaxial stress: optical and dilatometric investigation

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The stripe phase of the β-INC-α transformation of quartz under a uniaxial stress : optical and dilatometric investigation

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Résumé. — Un cristal de quartz soumis à une contrainte uniaxiale σ_{yy} montre l'existence d'anomalies entre les phases β et incommensurable $(3\,q)$ sur : la rotation et la dépolarisation de la lumière, la biréfringence et la dilatation. Ces anomalies révèlent l'existence de la phase monomodulée $(1\,q)$ récemment prévue théoriquement et découverte sous contrainte σ_{yy} par diffraction des neutrons. Elles permettent d'en préciser le diagramme de phase et de donner aussi celui-ci pour le cas σ_{xx}. Ces diagrammes révèlent que la phase $1\,q$ existe aussi à contrainte nulle sur un intervalle de quelques centièmes de K en température. En accord avec les prévisions théoriques cet intervalle varie plus vite avec σ_{yy} qu'avec σ_{xx} et la transition $1\,q \leftrightarrow 3\,q$ est du 1er ordre.

Abstract. — Anomalies of optical rotation, light depolarization, birefringence and dilatation of crystal quartz under σ_{yy} uniaxial stresses confirm the existence of an incommensurate $(1\,q)$ stripe phase, recently expected theoretically and discovered by neutron scattering, between the β and the INC $(3\,q)$ phases. The phase diagram is determined to a better resolution than with neutron diffraction. These anomalies allow us to obtain also the phase diagram of the $1\,q$ phase under σ_{xx} stresses. Both phase diagrams show the presence of the $1\,q$ phase over a small temperature range (a few hundreth K), even at zero stress. As expected from theory, the variation of its temperature interval is found to be larger with σ_{yy} stress than with σ_{xx} stress and the $1\,q \leftrightarrow 3\,q$ transition appears to be first-order.

1. Introduction.

The study of the effect of stresses on phase transitions in solids is of both theoretical and practical interest. In quartz, stresses cause the shift (10 K/kbar for σ_{xx} or σ_{yy} [1]) of the α-β (~ 573 °C) transition which influences all the properties down to ambiant temperature because the order parameter has not reached saturation [2]. Among other stress effects we may mention twinning [3] or detwinning [4], change of the morphology of the interface between the high and the low-temperature phases [5] and (the latest discovered [8]) induction of a new $1\,q$ INC phase between the β and the $(3\,q)$ incommensurate phases. This new phase is the subject of this paper. Let us recall that the β and the α phase are separated by an incommensurate (INC-$3\,q$) phase which exists in a temperature range of about 1.3 K on cooling [6, 7]. In appearance it resembles [10] a fine network of triangular columns (cross-section ~ 100 Å) parallel to the Z axis and it is explained [11] by the phenomenological Landau theory as the result of the superposition of 3 modulation waves 120° apart (Fig. 1a). When one adds to this theory [8] the effect of a uniaxial stress (σ_{yy} or σ_{xx}) — which breaks the symmetry of order 6 — a « $1\,q$ » phase between the β and the INC $(3\,q)$ phases is expected. According to the sign of $(\sigma_{xx} - \sigma_{yy})$ the wave vector of the $1\,q$ (INC) phase corresponds to one of the directions of the $3\,q$ (INC) wave vectors (Fig. 1c-d). This has been verified recently by neutron scattering but only with σ_{yy} stress [8] (Fig. 1c).

In this paper we first of all give the result obtained from optical investigations with σ_{yy} stress which allows us to determine the σ_{yy} phase diagram obtained with neutron diffraction. Secondly we investigate the σ_{xx} phase diagram to compare the

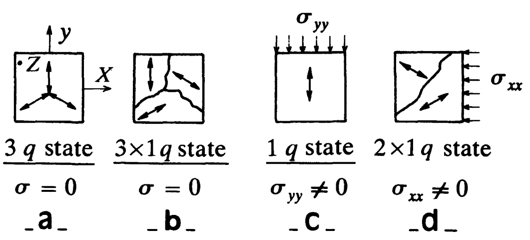

Fig. 1. — Possible wave vector position, in the X-Y plane, of the modulated incommensurate phase, according to the theory [8, 9]. The cases verified by experiments (neutrons or X-rays) are underlined.

previously evoked theory predicting a temperature range of the 1 q phase smaller than with σ_{yy} stress.

Experimental investigations involve rotatory power, optical polarisation, birefringence and dilatation measurements. In a preceding paper we have already shown that the β-INC transition is marked by a change of slope in dilatation and birefringence curves [6]. It is still more evident in rotatory power variation where it is also accompanied by a small peak of light depolarization [12].

The same techniques have been used in the present case to determine the stress dependence of these properties.

2. Apparatus.

The measurements were made on parallelepipeds ($7.5 \times 7.5 \times 30\ \mathrm{mm}^3$) of natural colourless and of good optical quality single quartz crystal with polished faces perpendicular to the crystallographic axis. The thermal apparatus has already been briefly described [1, 12] ; it allows measurements of dilatation (ΔL) with uniaxial compressive stress (by means of lever and weights) to be taken along the 30 mm height of the sample. A resistance thermometry bridge gives a temperature resolution better than 0.006 K. Two laser beams ($\lambda = 6\,328$ Å) are allowed to pass half way up and through the sample by mean of four holes of ~ 1.5 mm diameter. Optical rotation ($\Delta R = \rho \cdot d$; $d = 7.5$ mm) and light polarization ($I_\perp$) are measured along the Z axis using the method previously described [12] (the exit face of the sample is cut at an angle of $\sim 18'$ with respect to the entry face in order to reduce interference effects). The values of the phase birefringence $\varphi = \pi\, \Delta n \frac{\ell}{\lambda}$ ($\Delta n =$ birefringence, $\ell =$ 7.5 mm) were measured in a direction perpendicular to the Z axis (at a small angle of about 3° to avoid interference effects) by the de Senarmont method using an automatic device. ΔL, ΔR, $\Delta I_\perp$ and $\Delta\varphi$ are continuously recorded on $X - Y_1 - Y_2$ recorders with the temperature on the X axis.

Stress homogeneity was checked at room temperature from birefringence (photo-elastic effect) point-by-point exploration of the whole sample. On the horizontal (lasers) plane we find an inhomogeneity of about 3 % increasing to approximatively 10 % under the stainless steel piston which supplies the pressure (contact with a gold foil 0.1 mm thick). This residual inhomogeneity (very sensitive to the centering of the sample) appears to be intrinsic both from the geometric form of the sample and boundary conditions of stress application. At ambiant temperature we also discovered that the best extinctions on both directions are obtained under the best homogeneity stress conditions. These best values of extinction are taken as references to judge the quality of stress homogeneity at higher temperatures. It was thus necessary, in order to maintain stress evenness, to add two small jacks acting on the low piston to counter balance the deformation induced in the apparatus by large temperature or stress variations.

3. Results.

We will first present the results obtained with σ_{yy} stresses and then with σ_{xx} stresses. All curves are obtained with a typical temperature drift < 0.03 K/min and for discrete values of the stress (our apparatus does not allow us to pass continuously from $\sigma \equiv 0$ to $\sigma \neq 0$).

3.1 σ_{yy} STRESSES. — Figure 2a illustrates some selected examples of the evolution under stress of the dilatation in the β-INC region which is defined on the main (α-INC) hysteresis cycle shown (dotted lines) at small stress (10 bars) with a vertical reduction of four. For small stresses we see the usual change of slope previously [6] identified as the $\beta \leftrightarrow$ INC transition. While σ_{yy} increases a second change of slope appears which delimits a region of increasing temperature width with a nearly constant expansion coefficient. The birefringence variation (Fig. 2b) looks like the dilatation variation (they are generally proportional in quartz [13]) but with more details : a remarkable linearity between Ti_1 and Ti_3 as a function of the temperature ($\frac{\mathrm{d}\varphi}{\mathrm{d}T}$ decreases from 38°/K at zero stress to 26°/K at 700 bars) and, in addition, evidence of a small « vertical » discontinuity at Ti_3. This is more apparent at medium stress (291 bars) as shown on a large scale in figure 3b where one can also distinguish another small « vertical » discontinuity at Ti_1 which however disappears at higher stresses. In figure 3b we have also plotted (dotted line) the birefringence variation recorded at zero stress (with adequate ΔT and $\Delta\varphi$ shifts). The two curves can be superimposed except in the linear region where they intersect. This conclusion applies to all studied σ_{yy} stresses.

Rotatory power (ΔR) and light depolarization ($I_\perp$) are shown on the left of figure 2c-c′ with small

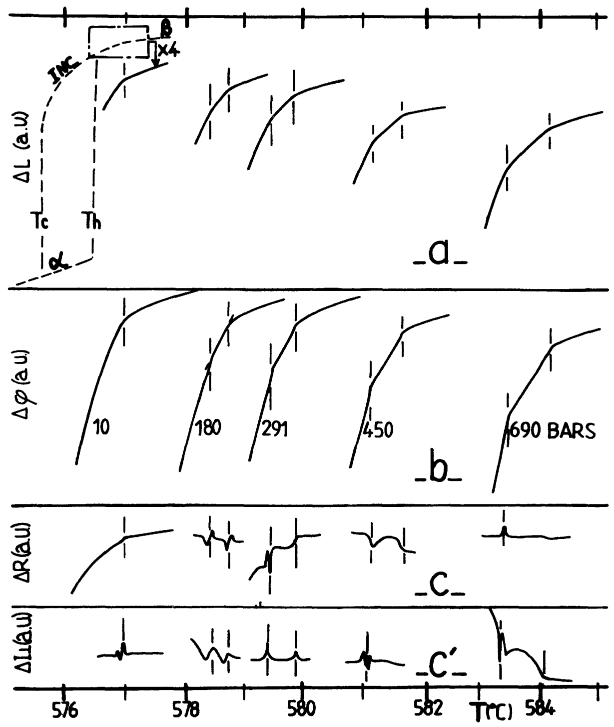

Fig. 2. — The temperature (cooling) dependance (in the β-INC region) of the dilatation ΔL (a) the birefringence $\Delta\varphi$ (b) the rotation ΔR (c) and the depolarization $\Delta I_{\perp}$ (c′) of the light propagating along the Z axis for some values of σ_{yy} (bars). The main (α-INC) hysteresis cycle is shown (a) (dotted lines) with a vertical reduction of four.

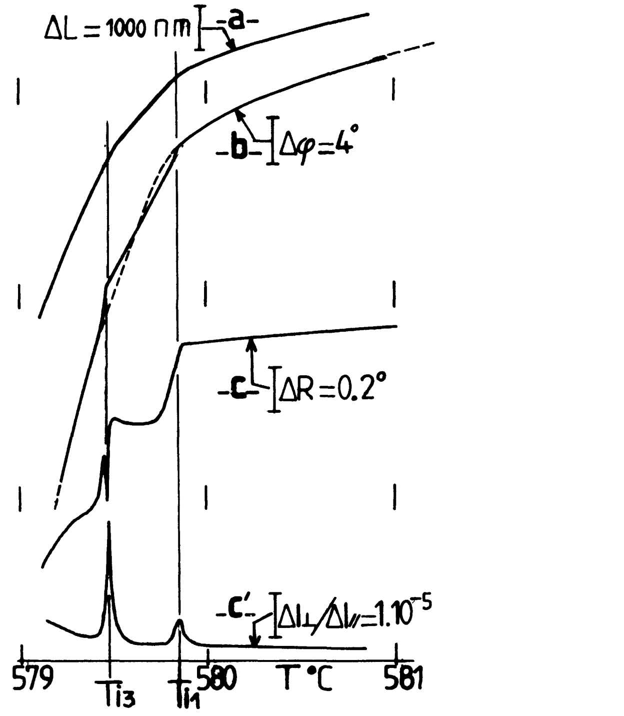

Fig. 3. — Example at medium σ_{yy} (291 bars) stress (on larger scale than Fig. 2) of the temperature dependance (cooling) of the dilatation ΔL (a) the birefringence $\Delta\varphi$ (b) the rotation ΔR (c) and the depolarization $\Delta I_{\perp}$ (c′). The dotted line on (b) is the birefringence variation (with adequate ΔT and $\Delta\varphi$ shifts) recorded at zero stress.

(10 bars) stress : β-INC transition is marked by an angular point on ΔR and the appearance of two small peaks on $I_{\perp}$.

At higher stress the rotatory power effect is superimposed on photoelastic induced birefringence. The emergent beam is generally elliptically polarized [14] — following an oscillating function of the stress (*) — so that our extinction method of detecting variation of rotatory power gives us in fact the rotation (ΔR) of the ellipse while the residual light ($I_{\perp}$) after the analyser gives the ellipticity.

To preserve the sensitivity of the automatic apparatus it is sometimes better to interpose a $\lambda/4$ plate (the effect of which is to interchange ΔR and $\Delta I_{\perp}$) in order to reduce the value of $I_{\perp}$. This operation is carried out only once in the β phase, without readjustment during temperature scans. Because we are interested only in the anomalies of the ΔR and $\Delta I_{\perp}$ curves the presence of the $\lambda/4$ plate is not subsequently shown.

Figure 2c-c′ shows some aspects of the two anomalies which appear at Ti_1 and Ti_3 under σ_{yy} stress (sometimes one of those anomalies is difficult to distinguish on one of these curves but both curves always allow Ti_1 and Ti_3 to be defined. Figure 3c-c′ shows that the peaks correspond to the vertical discontinuities, on the birefringence curves (Fig. 3b). As shown in figure 4a-a′ these peaks are particularly useful to determine Ti_1 and Ti_3 at low stress at which the anomalies on the birefringence curves are weak (Fig. 4b). We also observe that the peaks remain visible (although broadening) in spite of an inhomogeneous stress distribution (induced by the jack or by bad setting) while the anomalies on the birefringence and dilatation curves are smoothed out. The dotted lines in figure 4 show, for example at 52 bars, a heating curve obtained after cooling within the INC ($3\,q$) phase. We note a hysteresis of 0.012 K at Ti_3 (which increases to 0.03 K at 700 bars) while there is no hysteresis at Ti_1. (Sometimes a very small hysteresis (0.006 K) appears at Ti_1 and only for medium stress). We also note hysteresis (0.02 K) during the INC ($3\,q$) phase

(*) Starting, for instance, from formulae given in [15], the ellipticity χ of the transmitted light is $\sin 2\chi = \sin\left[2 \operatorname{arctg}\left(\frac{\rho d}{a\sigma}\right)\right] \sin^2\sqrt{(a\sigma)^2 + (\rho d)^2}$ with $(a\sigma)$ is the induced phase angle birefringence, a a photoelastic coefficient. In our experiment we find $\chi = 0$ for $\sigma = 0$; 126 ; 512 bars.

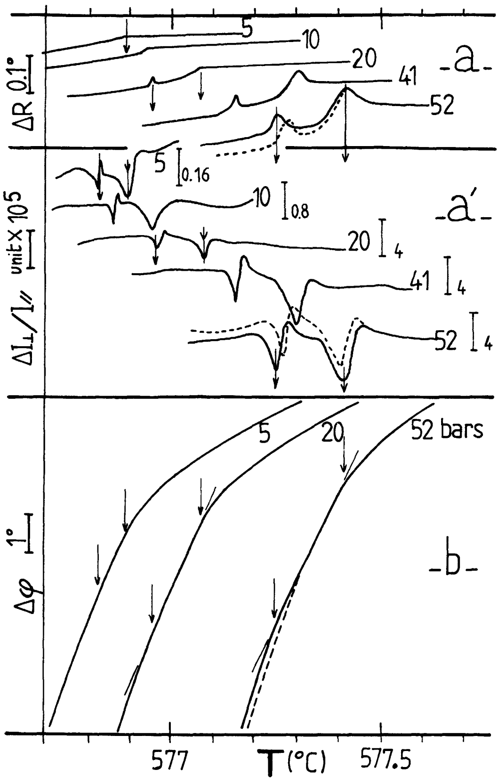

Fig. 4. — The evolution under low σ_{yy} stresses (5, 10, ... bars) of the anomalies which mark the $1\,q$ phase. Optical rotation ΔR (a), light depolarization $\Delta I_{\perp}$ (a'), birefringence $\Delta\varphi$ (b) obtained in cooling — dot line : example with heating (after cooling in the INC ($3\,q$) phase).

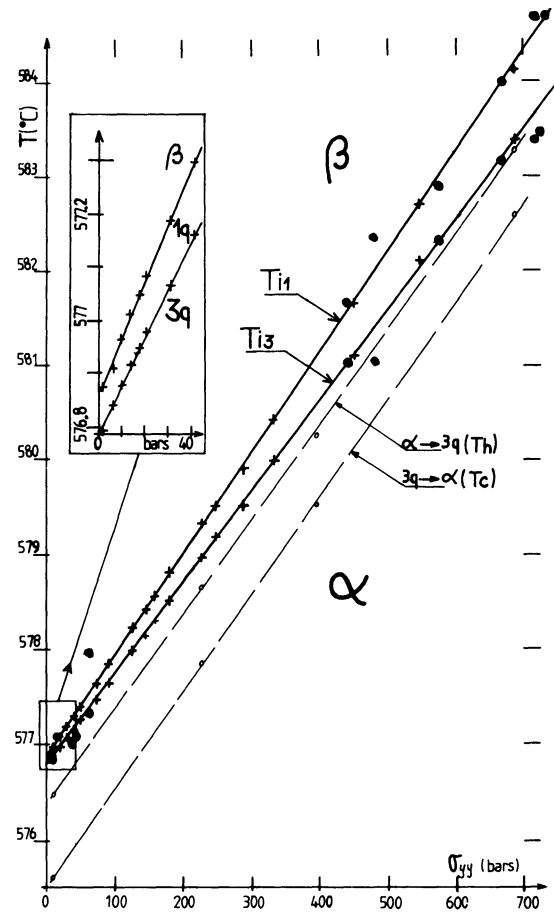

Fig. 5. — Phase diagram $[Ti_1(\beta \rightarrow 1\,q),\ Ti_3(1\,q \rightarrow 3\,q)]$ of the $1\,q$ phase under σ_{yy} stresses : + optical measurements (this work) ; • from neutrons [8] [the stress scale of [8] is corrected to adjust the T_c curves (evident mistake in the stress calibration) and the temperature is adjusted at low stress (thermometers calibration)].

which is known to be due to pinning of the incommensurate modulation by defects [16].

The change of slope on the dilatation and birefringence curves together with the anomalies in light polarisation and rotation are signs of the presence of a supplementary phase between the β and INC ($3\,q$) phases. To compare our results with neutron scattering results [8] under σ_{yy} stress, we have plotted a phase diagram with Ti_1 and Ti_3 temperatures (*) (Fig. 5) together with points determined by neutron diffraction : the agreement in the results leads us to conclude that Ti_1 and Ti_3 are the limits of the $1\,q$ phase. The optical measurements are however more accurate and enable us to deduce unambiguously that this $1\,q$ phase also exists at zero stress over a temperature range of about 0.07 K.

3.2 σ_{xx} STRESSES. — In this case we also clearly found an intermediate stress-induced phase, as the preceding effects described with σ_{yy} are also observed. However the $Ti_1 - Ti_3$ temperature difference is smaller, and we therefore had greater difficulty to observe it, especially by birefringence and dilatation studies. Figure 6 shows the variation of ΔR, $\Delta I_{\perp}$, $\Delta\varphi$ and ΔL at medium (316 bars) stress (to compare with Fig. 3 note that the temperature scale is expanded by a factor of two). On the birefringence curve it is also possible to note a small inflexion (which disappears at low and high stress) at Ti_3, reminiscent of the similar discontinuity under σ_{yy}. In general we find the same temperature hysteresis at Ti_1 and Ti_3 with variable values ($\sim 0.02 \pm 0.02$ K) as a function of stress, depending also on the depth of the excursion into the $3\,q$ phase. In figure 7 we plot the stress dependence of Ti_1 and Ti_3 which gives us (following the conclusion from σ_{yy} stresses) the phase diagram of the ($1\,q$) σ_{xx} stress-induced phase. We deduce also in this case the presence of the $1\,q$ phase at zero stress over a ~ 0.1 K temperature interval. We note that within

(*) We also report some values of the T_c and T_h main $\alpha \leftrightarrow$ INC transition temperatures which show a decrease of the width of the main hysteresis cycle with increasing σ_{yy} stress.

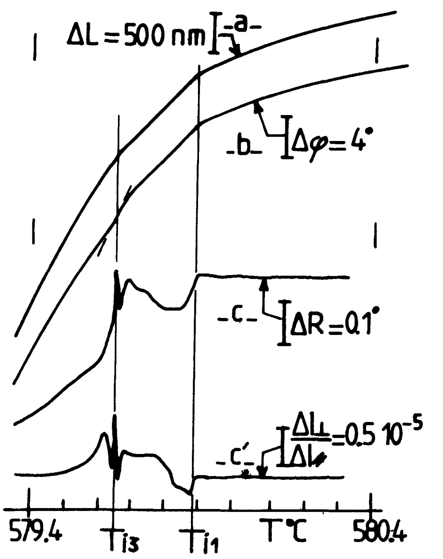

Fig. 6. — Exemple at medium σ_{xx} (316 bars) stress of the temperature (cooling) dependence of the dilatation ΔL (a), the birefringence $\Delta\varphi$ (b), the rotation ΔR (c) and the depolarization $\Delta I_{\perp}$ (c′).

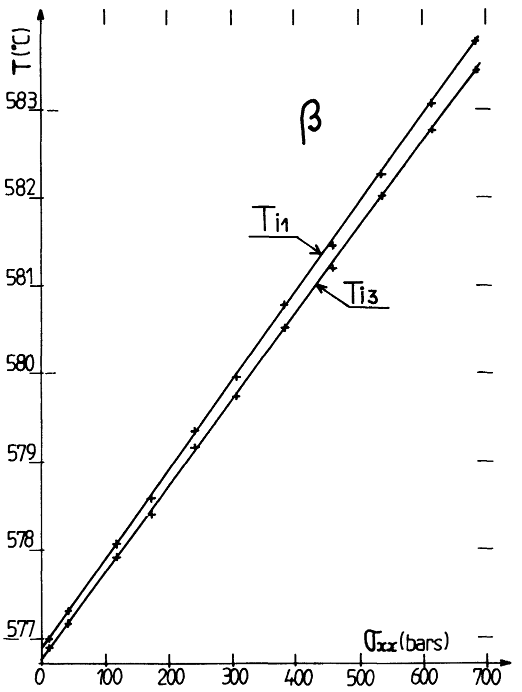

Fig. 7. — Phase diagram $[Ti_1(\beta \to 1\,q),\ Ti_3(1\,q \to 3\,q)]$ of the $1\,q$ phase under σ_{xx} stresses.

experimental uncertainty the slopes of the $Ti_3(\sigma_{xx})$ transition line and of the $Ti_3(\sigma_{yy})$ transition line are the same. Figure 8 shows that the range of existence of the $1\,q$ phase is larger (about two at high stress) with σ_{yy} than with σ_{xx}. Both cases exhibit linear variation, except for low stresses where a small deviation is visible.

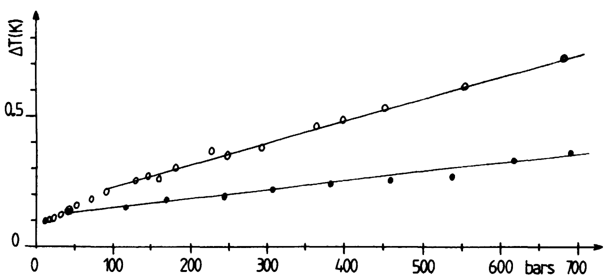

Fig. 8. — The temperature range ($\Delta T = Ti_1 - Ti_3$) of existence of the $1\,q$ phase as a function of σ_{yy}(O) or σ_{xx}(.).

4. Discussion.

— Although the dilatometric and birefringence variations are roughly similar, the details which additionally appear in birefringence curves can be explained by the fact that stress and temperature inhomogeneities are much smaller in the path of the light beam than in the whole sample height involved in the dilatation measurements ;

— concerning the $1\,q \leftrightarrow 3\,q$ transition one can say that the discontinuities observed clearly at medium stress (~ 1/60 of the main $\alpha \leftrightarrow$ INC transition discontinuity) together with hysteresis are in favor of a 1st order transition in agreement with theory [8]. We also find that the discontinuity increases (with a broadening probably due to stress inhomogeneity) with applied σ_{yy} stress. This could explain why it is difficult to observe it at low stress on birefringence curves and was not detected in a preceding paper [6]. On the other hand the depolarization peak becomes very narrow and the shape of the anomalies depends on the exact experimental conditions which could explain why we did not observe it previously [12]. A first-order transition explains the anomalies in light polarization and rotation as being due to the passage of the front phase which induces a gradient stress from volume discontinuity ;

— concerning the apparent differences in the shape of the anomalies induced by σ_{yy} or σ_{xx}, this could be due to the narrower range of existence of the $1\,q$ phase in the latter case and also probably to the difference in the nature of the $1\,q$ states (in particular the possible existence of domains walls for compressive σ_{xx} stresses separating the $1\,q$ regions (cf. Fig. 1d)) ;

— concerning the $1\,q \leftrightarrow \beta$ phase transition it is much more difficult reach a conclusion regarding the order of this transition : the very small thermal hysteresis is only observed at middle σ_{yy} stresses and, furthermore, the very small discontinuity in birefringence also disappears at higher stresses. The peaks of light depolarization and rotation always remain up to zero stress. However the possibility of a 2nd-order phase transition cannot be ruled out, since a step-like discontinuity of elastic constant also exists in this case and can lead to non-uniform sample properties along the light path ;

— a larger range of existence of the $1\,q$ phase with σ_{yy} than with σ_{xx} is in qualitative agreement with theory [8] which however does not predict a $1\,q$ phase at zero stress. As already emphased [8] « the role of critical fluctuations and quenched defects could be relevant in this case ». Likewise the role of defects could explain the non linearity at low σ_{yy} or σ_{xx} stresses (the $3 \times 1\,q$ (Fig. 1b) phase could exist even at small stress as recently observed by X ray scattering [17]).

5. Conclusion.

We have shown how the $1\,q$ phase previously identified by neutron measurements (under σ_{yy} stress) is also obvious from dilatation curves and optical measurements. The $1\,q$ phase between the $3\,q$ and β phases is marked :

— on dilatation and birefringence curves by two changes of slope (one already known at $1\,q \leftrightarrow \beta$ and a new one at $1\,q \leftrightarrow 3\,q$) separated by a straight line ;

— on birefringence ($\Delta\varphi$) curves : the straight line is limited by a small (increasing with σ_{yy} stress) discontinuity at $1\,q \leftrightarrow 3\,q$ and sometimes, with σ_{yy}, a very small discontinuity at the $1\,q \leftrightarrow \beta$ transition ;

— in light polarisation and rotation along the Z axis by two anomalies (often peaks) at $1\,q \leftrightarrow 3\,q$ and $1\,q \leftrightarrow \beta$ transitions.

We have been able to determine more accurately the phase diagram with σ_{yy} stress and to give the phase diagram for the σ_{xx} case for the first time. In both cases, the existence of the $1\,q$ phase at zero stress is clearly established (similar conclusions have been very recently reached from neutron diffraction [18] and elastic light scattering [19]). We are in qualitative agreement with the Landau theory [8] concerning the relative (larger) variation of the temperature existence interval of the $1\,q$ phase under σ_{yy} and σ_{xx} stress and the order (1st) of the $1\,q \leftrightarrow 3\,q$ transition. However this theory does not lead to a $1\,q$ phase at zero stress.

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